

## TDDFT方法研究两个基于Michael反应的氰离子传感器的不同传感机理

### TDDFT Study on Different Sensing Mechanisms of Similar Cyanide Sensors Based on Michael Addition Reaction

摘要点击 221 全文点击 121 投稿时间: 2011-3-2 采用时间: 2011-4-11

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doi: 10.1088/1674-0068/24/03/305-310

中文关键词 [传感器](#) [荧光](#) [氰离子](#) [传感机理](#) [含时密度泛函理论](#) [Michael加成反应](#)

英文关键词 [Sensor](#) [Fluorescence](#) [Cyanide](#) [Sensing mechanism](#) [Time-dependent density functional theory](#) [Michael addition reaction](#)

基金项目

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中文摘要

利用含时密度泛函方法计算了两个具有类似结构的传感器分子a和b的氰离子传感机理. 结果证实, 传感器分子a在基态和 $S_1$ 态下有着类似的几何构型. 在质子性溶剂水中, 氰离子能与传感器分子a发生Michael加成反应, 水溶液提供质子, 促使最终的 $\alpha,\beta$ -加成产物的生成. 而此加成产物在 $S_1$ 态下会发生构型变化, 导致荧光的猝灭. 传感器分子b的 $S_1$ 态与基态构型相比发生了构型扭转, 并且在非质子性溶剂乙腈中, 也可以与氰离子发生Michael加成反应. 由于乙腈

英文摘要

The solvents and substituents of two similar fluorescent sensors for cyanide, 7-diethylamino-3-formylcoumarin (sensor a) and 7-diethylamino-3-(2-nitrovinyl)coumarin (sensor b), are proposed to account for their distinct sensing mechanisms and experimental phenomena. The time-dependent density functional theory has been applied to investigate the ground states and the first singlet excited electronic states of the sensor as well as their possible Michael reaction products with cyanide, with a view to monitoring their geometries and photophysical properties. The theoretical study indicates that the protic water solvent could lead to final Michael addition product of sensor a in the ground state, while the aprotic acetonitrile solvent could lead to carbanion as the final product of sensor b. Furthermore, the Michael reaction product of sensor a has been proved to have a torsion structure in its first singlet excited state. Correspondingly, sensor b also has a torsion structure around the nitrovinyl moiety in its first singlet excited state, while not in its carbanion structure. This could explain the observed strong fluorescence for sensor a and the quenching fluorescence for the sensor b upon the addition of the cyanide anions in the relevant sensing mechanisms.

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主管: 中国科学技术协会 主办: 中国物理学会 国际代理发行: 英国物理学会

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